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Synthesis and structure of tetrathiophene with a chiral 1,1′-binaphthyl kink†

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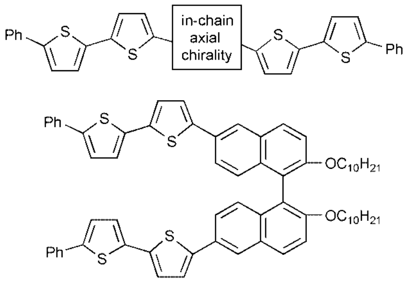
A chiral oligothiophene, possessing in-chain chirality, was prepared and its racemate was characterized by single crystal X-ray crystallography; the in-chain chiral 1,1′-binaphthyl moiety interrupts the π-conjugation and affects the solid state properties of the oligothiophene.

Oligothiophenes are attracting attention as functional materials for (opto)electronic devices.[1,2] Soluble oligothiophenes are especially valuable in applications where reproducible high chemical purity is essential and recently developed solution printing techniques can be utilized, *e.g.* in ‘plastic electronics’ based upon field effect transistors.[2] The well-defined oligomers are also studied as models for the parent polymers.[3] The crystal structures of a number of oligothiophenes have been reported.[2,4]

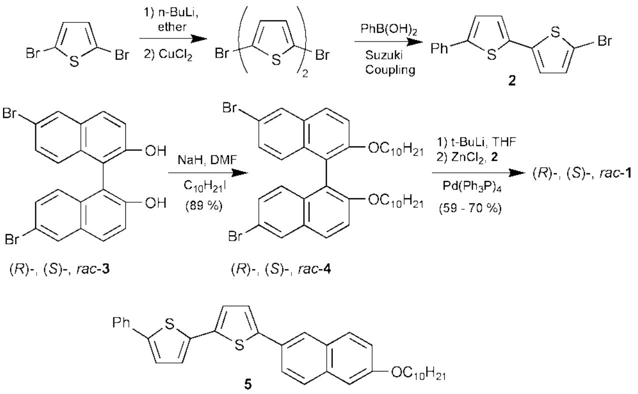
The introduction of chirality into the oligo- or polythiophenes is expected to provide an additional engineering tool for these materials, arising not only from intrinsic chirooptical and chiroelectronic properties but also from diastereomeric interactions in the solid state.[5,6] Polythiophenes with various chiral pendant groups and in-chain 1,1′-binaphthyls have been reported.[7,8]

We report on the synthesis and single crystal X-ray structure determination of 6,6′-bis(5-phenyl-2,2′-bithiophen-5′-yl)-2,2′-bis(decyloxy)-1,1′-binaphthyl (**1**), a chiral oligothiophene, possessing in chain chirality.



(*R*)-, (*S*)-, and *rac*-**1**

The convergent synthesis of (*R*)-, (*S*)-, and *rac*-**1** is based upon the connection of two achiral modules **2** to the chiral module **4**, which is available in the (*R*)-, (*S*)-, and racemic-forms. 5′-Bromo-5-phenyl-2,2′-bithiophene (**2**) is obtained in two steps: (1) 2,5-dibromothiophene is treated with 1 equiv. of n-BuLi in diethyl ether, followed by oxidation with CuCl$_2$ to give 5,5′-dibromo-2,2′-bithiophene,[9] (2) Suzuki coupling of phenylboronic acid in the presence of an excess of 5,5′-dibromo-2,2′-bithiophene gives **2** in 68% yield.[10,11] 6,6′-Dibromo-2,2′-bis(decyloxy)-1,1′-binaphthyls (**4**) are prepared according to the previously published procedures for analogous bis(dodecyloxy) derivatives by etherification of 6,6′-dibromo-1,1′-binaphthyl-2,2′-diols (**3**) with iododecane in the presence of NaH in DMF.[12] The modules **2** and **4** are linked *via* Negishi coupling providing (*R*)-, (*S*)-, and *rac*-**1** in 59–70% yields (Scheme 1).[13,14] Analogous synthetic procedures were used to obtain the model bithiophene **5**.



Scheme 1 Synthesis of (*R*)-, (*S*)-, and *rac*-**1**, and the structure of the reference compound **5**.

Orange, block-shaped crystals of *rac*-**1** suitable for X-ray diffraction experiments were grown by slow evaporation of the solvent from a hexane–chloroform solution.[15] The structure displayed by **1** is that of a twisted binaphthyl with the alkoxy chain of one naphthyl unit packing against the naphthyl–thiophene–thiophene–phenyl π-system of the other half of the molecule (Fig. 1). Each of the π-systems is nearly planar, exhibiting small interplanar twist angles.[16] Possible 2-fold symmetry about an axis perpendicular to the C(1)–C(25) binaphthyl linkage is broken by the differing conformations displayed by the alkoxy chains. The difference is a single torsion angle. The conformation about the C(2A)–C(3A) bond is *trans* [C(1A)–C(2A)–C(3A)–C(4A) = −176.2(4)°], whereas the C(2B)–C(3B) conformer is *gauche* [C(1B)–C(2B)–C(3B)–C(4B) = −68.8(5)°]. The remainders of both chains are in all-*trans* conformations. Because of the difference in conformation, the plane containing C(2B–10B) lies parallel to the adjacent π-system, while the C(2A–10A) plane is essentially perpendicular to the adjacent π-system. Both chains lie in close contact with

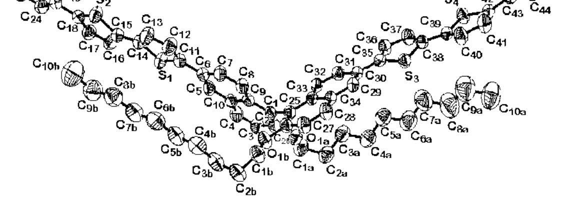


Fig. 1 The conformation for the crystal structure for *rac*-**1**. Ellipsoids are shown at 50% probability.

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† Electronic supplementary information (ESI) available: synthesis and characterization data for **1**, **2**, **4**, and **5**; crystal packing plots for *rac*-**1**. See http://www.rsc.org/suppdata/cc/b0/b007355p/

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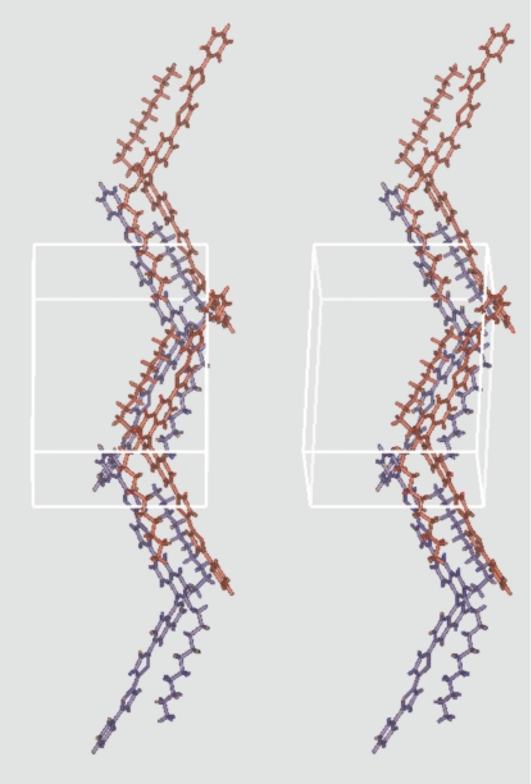

Fig. 2 Crystal packing for *rac*-**1**: stereoview (approximately *bc*-plane) of the tetramer fragment of the zig-zag chain extending along the *c*-axis. The enantiomers are color-coded.

each π-system, with alkyl hydrogens pointing towards the π-systems. We suggest that this interaction influences the conformation of the binaphthyl core. The binaphthyl twist displayed [C(9)–C(1)–C(25)–C(33) = 107.3(3)°] is larger than that observed in binaphthyl (101.4°)[17] and most other 2,2-disubstituted binaphthyls, *e.g.* 2,2′-dihydroxy-1,1′-binaphthyl (92.5°)[18] and 2,2′-bis(bromomethyl)-1,1′-binaphthyl (86.8°).[19]

For the discussion of the crystal packing in *rac*-**1**, the two π-conjugated moieties of **1** may be viewed as a molecular hinge. The phenyl–bithiophene–naphthyl moieties from the mirror image enantiomers form a quasi-one-dimensional zig-zag chain extending along the *c* axis (Fig. 2). Such a chain of molecular hinges is facilitated by the alternating enantiomers. Along the *a* axis, the chains pack side-by-side to form quasi-two-dimensional zig-zag layers, which pack on top of each other in a ‘lock-and-key pattern’. The homochiral π–π interactions are negligible as the phenyl–bithiophene–naphthyl moieties form alternating stacks with the alkyl chains.

With bithiophene **5** as a reference, UV-vis spectra of **1** reveal that the nonplanar chiral binaphthyl moiety highly attenuates the π-conjugation.[8] The broad π–π^* transitions (λ_{max} = 393 nm) for **1** and **5** are essentially superposable, except for the molar absorptivities, which in **1** are approximately twice those in **5** (log ε_{max} = 4.9 and 4.6). The fingerprint regions of the IR spectra of solid (*R*)- and (*S*)-**1** show small differences compared to the IR spectrum of *rac*-**1**. Also, the melting point of *rac*-**1** is about 40–50 °C higher than those for the (*R*)- and (*S*)-enantiomers, suggesting the presence of a racemic compound.[20] Moreover, the melting point of bithiophene **5** is even higher, about 95 °C above *rac*-**1**. The solubility in chloroform (g mL^{-1}) increases in the following order: (*S*)-**1** (2×10^{-1}) > *rac*-**1** (8×10^{-4}) > **5** (2×10^{-5}), *i.e.* the opposite order to the melting points. These significant differences in solubilites are of importance for the solution processability of oligothiophenes.

In summary, the introduction of chirality into the oligothiophene chain leads to significant differences in solid state properties between stereoisomers and should be an important factor in their solution processability. Further studies on crystal packing and materials properties of chiral molecular hinges in the neutral and doped states are in progress.

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